

Chemical investigations of element 108, hassium (Hs)

Ch.E. Düllmann^{1,2}

¹ Lawrence Berkeley National Laboratory, Berkeley, USA

² University of California, Berkeley, USA

CEDuellmann@lbl.gov

Introduction

The basic aim of chemistry experiments of transactinide elements (TAN) is to establish their place in the periodic table of the elements, i.e. to determine if their chemical behavior is similar to the one of supposed homologs. In this contribution I will try to give an overview of all chemical experiments on element 108, hassium (Hs) that have been reported to date.

Based on the systematics of the periodic table, Hs is expected to be a member of group 8 and therefore homologous to osmium (Os) and ruthenium (Ru). As a member of the transactinide series, its experimental investigation is complicated by low production cross-sections and short half-lives. It has therefore been successfully investigated only recently. Already in the seventies of the last century, several authors mentioned the tetroxides of the two heavier group 8 elements, Ru and Os, to be very outstanding compounds with respect to their unusually high volatility. A possible HsO₄ was considered suitable for isolating Hs from unwanted by-products of the nuclear production reaction [1-4]. While RuO₄ is rather unstable, OsO₄ is well-known to be a stable compound and is widely used in organic chemistry. Recent theoretical calculations on the electronic structure and properties of Hs [5,6] predict the formation of a stable HsO₄ whose properties should be similar to the ones of OsO₄. This is in agreement with an extrapolation of the trend established in group 8 of the periodic table by Ru and Os [7]. All of the reported experiments on the chemistry of Hs therefore aimed at a formation of this compound.

Hs was discovered in 1984, when Münzenberg et al. reported the observation of a correlated decay-chain from ²⁶⁵Hs formed in the nuclear reaction ⁵⁸Fe(²⁰⁸Pb; n) [8]. However, its half-life is only 1.55 ms, too short for a successful chemistry experiment. Early chemistry experiments therefore aimed at the production and detection of more neutron-rich Hs isotopes which were expected to be longer-lived. In some experiments, a nuclide with a higher Z was produced which was expected to subsequently decay to an isotope of element 108. In 1996, ²⁶⁹Hs (T_{1/2}~10 s) was discovered [9], and it was this relatively long-lived isotope which was used in the recent experiments.

In the following, all experiments on the chemical investigation of Hs are presented in a chronological order.

Early experiments

The first attempts to chemically identify elements 108, which had been discovered only one year earlier, were undertaken in Dubna in 1985. Spontaneously fissioning (SF) isotopes produced in the heavy-ion induced fusion reactions ⁴⁰Ar+²³⁵U (leading to ²⁷⁵110 as the compound nucleus, CN) and SF or α -decaying ²⁶⁷Hs produced in the ²²Ne+²⁴⁹Cf reaction (CN ²⁷¹Hs) were searched for [10,11]. ²⁶⁷Hs was believed to have a half-life on the order of 1 s. The nuclear reaction products were thermalized in a Ar/O₂ gas mixture and continuously swept out of the target chamber through a heated CaO filled column which acted as a filter to separate non-volatile transfer products as e.g. actinides, Ra, Fr, and Po. The volatile species were blown onto the surface of a Pb coated Si detector. At the opposite side an annular lavisan track detector was located for registering fission fragments.

In Berkeley, a set-up called the On-line Separation and Condensation AppaRatus (OSCAR) [12] was used for a search for α -decaying ^{272}Hs which was expected to be the electron capture daughter product of ^{272}Mt produced in the reaction $^{254}\text{Es}(^{22}\text{Ne}, 4n)$ [13]. Nuclear reaction products were transported with a KCl gas-jet to the chemistry setup where O_2 was added to the carrier gas. The aerosol particles were caught on a heated quartz wool plug where the transported species were converted to oxides. Non volatile transfer products remained in the reaction area while the volatile oxides were swept out by the gas flow and deposited on a silver disk which was cooled by liquid nitrogen (LN_2). Opposite of the metal disk, an annular Si surface barrier detector was mounted which registered α - and SF decaying nuclides adsorbed on the disk.

In all of these experiments, the decontamination from actinides and other interfering species was excellent. Nevertheless, no events that could be attributed to the decay of Hs were observed and upper limits of 100 pb for the production cross sections of α -decaying nuclides and 50 pb for SF decaying nuclides were established in the Dubna experiments and a limit of 1 nb was reported from the OSCAR experiment. As we know nowadays, the sensitivity of these early experiments was too low to yield positive results. Meanwhile, several isotopes that were unknown at that time were discovered and exhibited decay properties different from the ones assumed (and necessary for a successful experiment).

The IVO-COLD experiment

In 2001, the next attempt to chemically investigate Hs was undertaken by a large collaboration. A schematic of the set-up used is depicted in Figure 1.

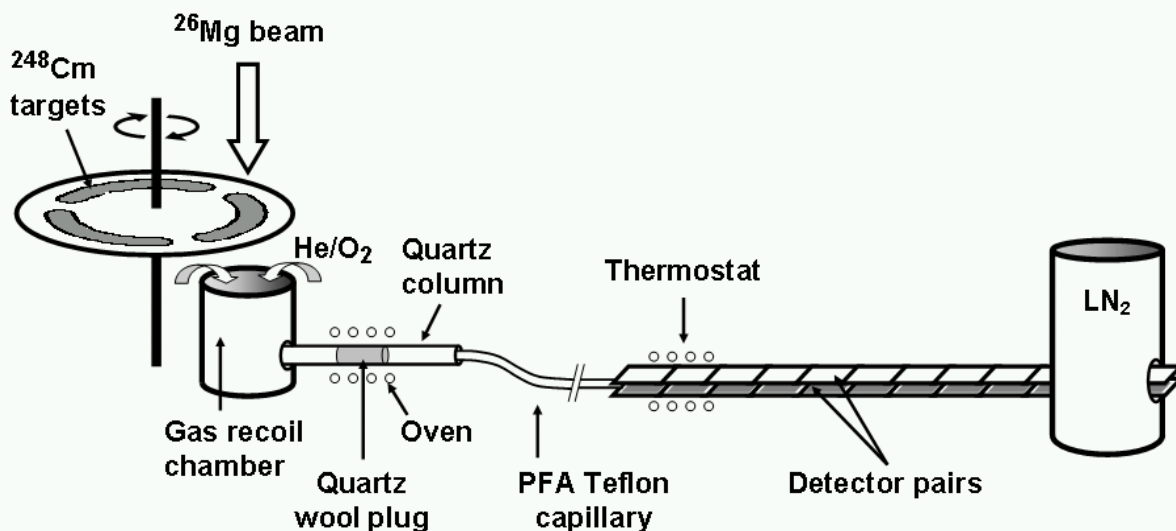


Figure 1. Schematic of the experimental setup in the IVO-COLD experiment. For explanations see text. Adapted from [14].

Relatively long-lived Hs isotopes were produced in the reaction $^{248}\text{Cm}(^{26}\text{Mg}; 5,4n)^{269,270}\text{Hs}$. Reaction products recoiling from the target were thermalized in a gas filled volume called the recoil chamber which was flooded with a He/O_2 mixture. The formed radionuclides were transported by the gas flow to a nearby oven kept at 600 °C where formation of the tetroxide took place. Hs was then transported through a PFA Teflon tube to the detection device in the form of HsO_4 . This technique was named In-situ Voaltization and On-line detection (IVO) [15]. The efficiency of IVO to forward formed short-lived Os

isotopes to the detection system was measured to be 60-90% in test experiments. The method of gas phase adsorption thermochromatography [16] was used to measure the deposition temperature of HsO_4 on the surface of a chromatography column. An on-line thermochromatography system has been developed at Berkeley [17] and an improved version called the Cryo-On-Line Detector (COLD) [14,18] has been built at the Paul Scherrer Institute in Switzerland. The chromatography column consisted of 12 pairs of PIN-diodes (Area: $1 \times 3 \text{ cm}^2$ each) forming a narrow rectangular channel with a spacing of 1.6 mm. PIN-diodes are suitable for registering α -particles and fission fragments. By means of a thermostat and a vessel containing LN_2 , a temperature gradient from -20 to -170 °C was established along the column. Deposition of HsO_4 was expected at a temperature lying between these two values. The overall efficiency of the IVO-COLD system was 30-50%.

Table 1. Observed correlated decay chains. Given are the energies of the observed events and the time difference between an event and the preceding one. The setup used did not allow for determining the lifetime of the mother events. Fission events are marked with an asterisk. Two asterisks identify SF events where only one fragment was registered. n_R is the probability of a chain to be of random origin not related to the decay of a Hs isotope. Det. indicates the detector unit in which the chain was observed. The last column gives the isotope to which the decay chain was assigned to.

#	E_1 [MeV]	E_2 [MeV]	Δt_2 [s]	E_3 [MeV]	Δt_3 [s]	E_4 [MeV]	Δt_4 [s]	n_R	Det.	Isotope
1	9.16	8.66	25.665	94+93*	0.199			$<8 \times 10^{-6}$	2	^{270}Hs
2	9.18	8.69	4.409	8.50	2.365	8.21	55.567	$<2 \times 10^{-6}$	3	^{269}Hs
3	-	8.72	-	53**	3.124			$<2 \times 10^{-4}$	4	$^{269/270}\text{Hs}$
4	8.97	8.64	11.911	94+92*	1.216			$<5 \times 10^{-5}$	4	^{270}Hs
5	9.10	8.68	9.325	94+85*	7.920			$<7 \times 10^{-6}$	3	^{269}Hs
6	8.88	8.90	17.078	8.50	0.846			$<7 \times 10^{-5}$	3	^{269}Hs
7	9.14	-	-	108**	42.615			$<4 \times 10^{-4}$	3	$^{269/270}\text{Hs}$

Data was acquired during 64.2 h and a total of 10^{18} particles passed through the target. The obtained α -spectra were very clean and exhibited only α -particle lines of ^{211}At and $^{219,220}\text{Rn}$ and their daughters. ^{219}Rn was added to the carrier gas to allow for an on-line calibration of the detectors. The correlation analysis revealed a total of seven correlated decay chains [19] which are given in Table 1. The distribution of Hs and Os in the temperature gradient tube is shown in Figure 2 which contains the merged thermochromatogram of $^{172}\text{OsO}_4$ ($T_{1/2}$: 19 s) and the events attributed to the decay of a Hs isotope.

The enthalpy of adsorption ΔH_{ads} of the species on the column surface material (silicon nitride, Si_3N_4) was extracted from the measured deposition distribution by using Monte Carlo simulations of the trajectories of single molecules as they move along the column under real experimental conditions [20] (see Fig. 2, solid lines). The only free parameter is the ΔH_{ads} of the compound on the stationary phase. The half-life of the nuclide is a crucial parameter in this procedure and since it has not yet been measured for ^{270}Hs , the ΔH_{ads} of the compound on the silicon nitride surface was evaluated using only the three decay chains attributed to ^{269}Hs which occurred in detector pair 3. Values of $\Delta H_{\text{ads}} = (-46 \pm 2) \text{ kJ/mol}$ (68% c.i.) for HsO_4 and $(-39 \pm 1) \text{ kJ/mol}$ for OsO_4 were deduced using a $T_{1/2}$ value of $(11^{+15}_{-4}) \text{ s}$ [9,21] for ^{269}Hs . This result points to HsO_4 as the transported species. The ΔH_{ads} value of OsO_4 of $(-39 \pm 1) \text{ kJ/mol}$ deduced from this experiment was in good agreement with earlier investigations using quartz surfaces [1,15,17].

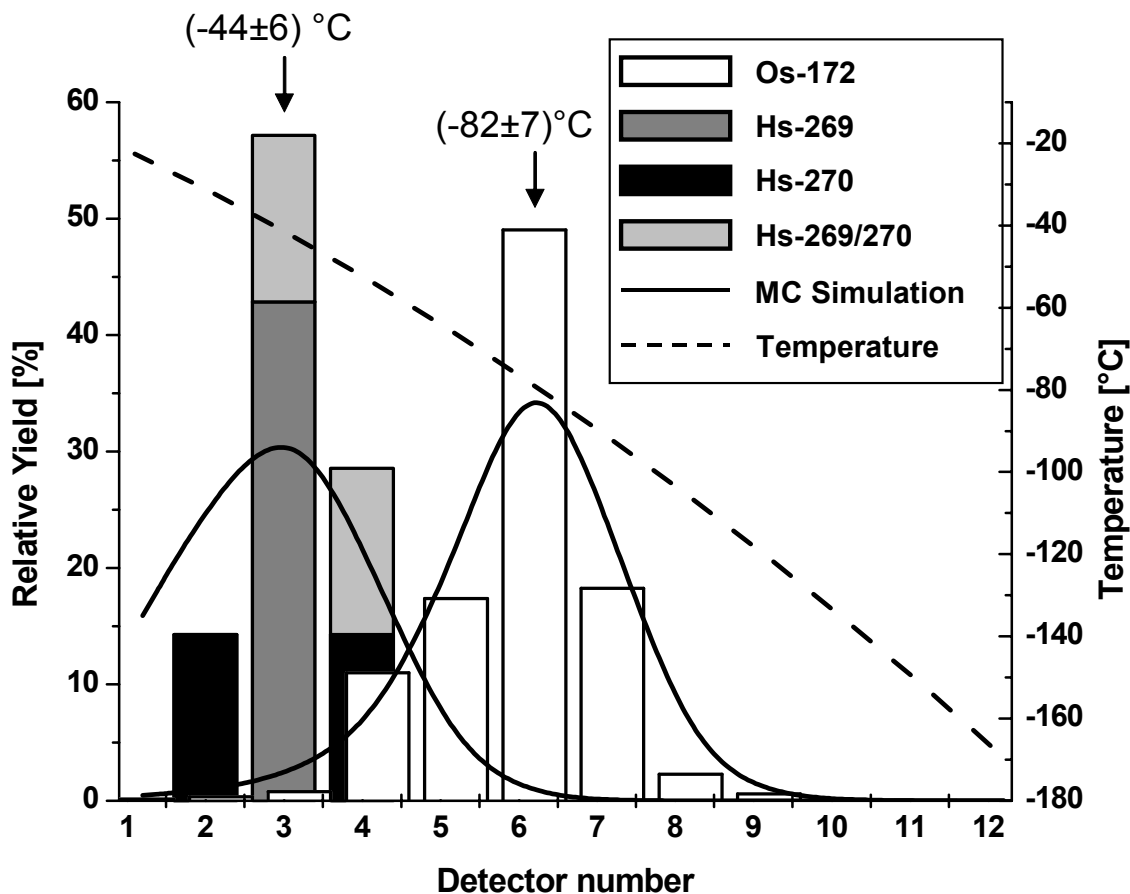


Figure 2. Merged thermochromatogram of HsO_4 and OsO_4 [14]. The deposition temperatures are indicated. Solid lines represent results of a Monte Carlo simulation. The dashed line indicates the temperature gradient. Adapted from [14].

The CALLISTO experiment

The most recent Hs experiment has been performed by a GSI - Univ. Mainz - JAERI collaboration. The setup used was named Continuously working Arrangement for for clusterLess transport of In-SiTu produced volatile Oxides (CALLISTO) [22] and is depicted in Figure 3. The goal of the experiment was the deposition of the volatile HsO_4 on a reactive substrate. OsO_4 is known to react with hydroxides forming osmates(VIII) of the composition $[\text{OsO}_4(\text{OH})_2]^{2-}$ and test experiments at GSI showed that carrier-free OsO_4 deposits on hydroxide surfaces with high yields [23]. Hs was produced using the same nuclear reaction as the IVO-COLD experiment, i.e. $^{26}\text{Mg}(^{248}\text{Cm}; 5,4n)^{269,270}\text{Hs}$. These isotopes were converted to HsO_4 immediately behind the target and transported to the chemistry device with the gas flow. HsO_4 was deposited on a thin layer of NaOH, presumably due to reduction according to $2\text{NaOH} + \text{HsO}_4 \rightarrow \text{Na}_2[\text{HsO}_4(\text{OH})_2]$, yielding a hassate(VIII) [24]. The detection system consisted of a narrow rectangular channel with the bottom coated with a thin-layer of NaOH. The top consisted of PIN-diodes allowing for registering α -particles and fission fragments in a 2π -geometry. A total of 4 of these detector boxes were available. Three were serially coupled while the fourth one was available for maintenance and coating.

The present status of the data analysis shows that formed HsO_4 was deposited on the first few centimeters of the NaOH covered channel. The preliminary results indicate one correlated α - α - α -decay chain and 5 α -SF chains which were attributed to the decay of a Hs isotope [25]. The distribution of the 6 decay chains in the detection system is similar to the one observed for Os. Thus, it appears likely that Hs reacts with the NaOH surface in a similar way as Os.

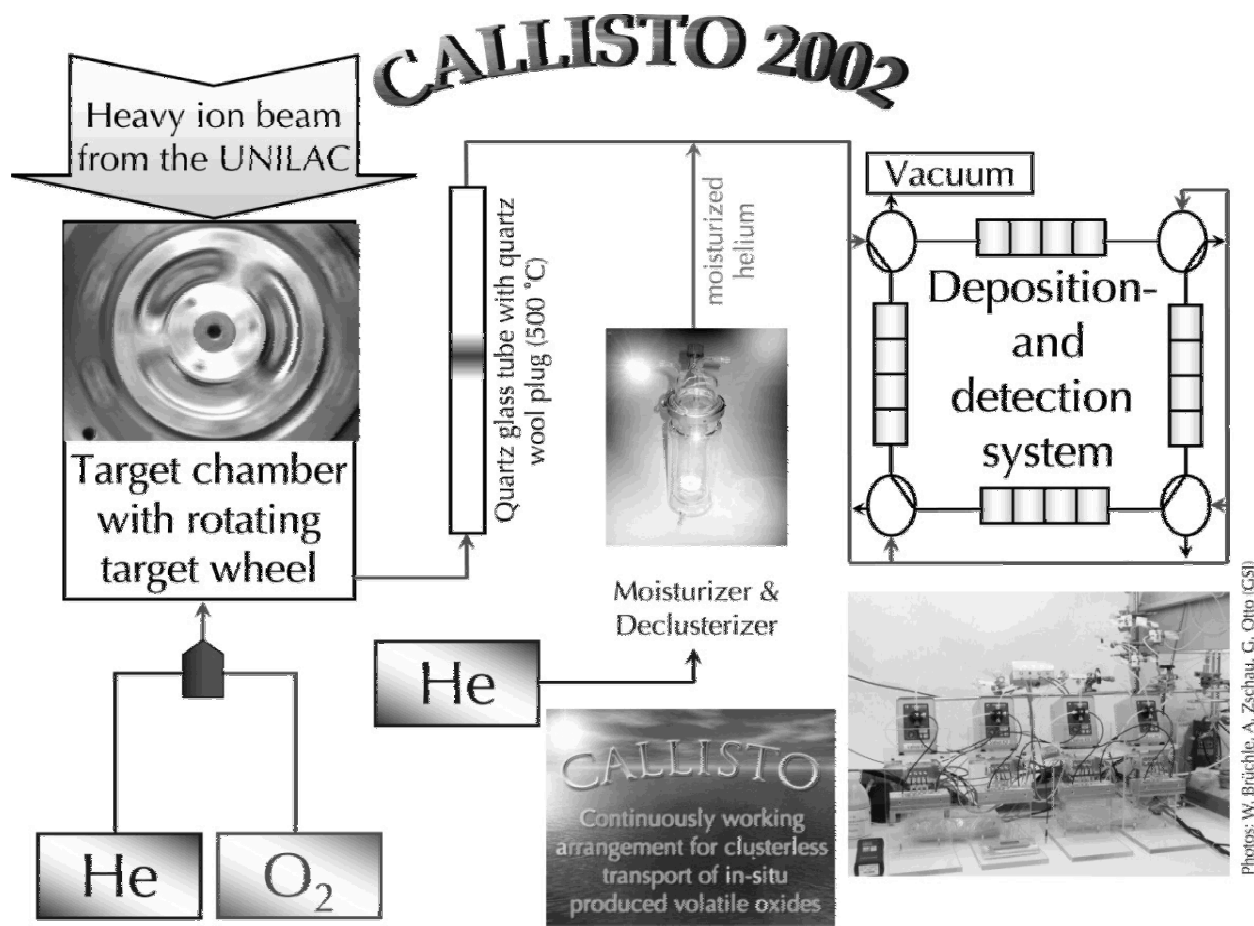


Figure 3. The CALLISTO setup [22]. For details see text. Figure courtesy of A. v. Zweidorf.

Conclusions

Currently, two experiments have successfully investigated the chemical behavior of Hs. In the first study, formation of a volatile oxide, presumably HsO_4 and its deposition on a dielectric surface was studied. It was found that the interaction was slightly stronger for HsO_4 than OsO_4 . Nevertheless, the findings justified the classification of Hs into group 8 of the periodic table. In the second experiment, the reaction of HsO_4 with a NaOH surface was investigated and evidence for the formation of a hassate(VIII) was obtained. Therefore, Hs has revealed an analogous behavior to Os also in this system.

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